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# A CONTRIBUTION TO THE NATURAL HISTORY OF MARL.[1]

BOTANISTS have long been familiar with the fact that, in some regions, aquatic plants of all, or nearly all, types are covered with a more or less copious coating of mineral matter, while in other localities the same types of plant life are free from any trace of such covering. In New England, for example, plants growing in the water are generally without such coating, while in Michigan and adjoining states it is generally present. In many lakes and streams the mineral deposit on the stems and leaves of the higher plants is very noticeable, and nearly all vegetation growing in the water is manifestly an agent of precipitation of mineral matter.

Various writers in Europe[2] and America[3] have called attention to the influence of the low types of plants growing in and around hot springs and mineral springs, on the formation of silicious sinter, calcareous tufa, and other characteristic deposits of such springs, and the connection between the beds of calcareous tufa which are sometimes formed about ordinary seepage springs whose waters carry considerable calcareous matter in solution and certain species of moss has been suggested, but so far as the writer knows, no one has given attention to the possible relation of vegetation to the more or less extensive beds of the so-called marl, found about, and in, many of the small lakes in Michigan and the adjacent states. As has been pointed out elsewhere, "Marl" is made up principally of nearly pure calcium carbonate, "carbonate of lime," with greater or less admixture of impurities. When dry and pure, it is white or slightly cream colored, coarsely granular to finely powdery, very loosely coherent and effervescing freely in acids. On dissolving it particles of vegetable and other organic and insoluble matter are found scattered through the solution.

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[1] Printed by permission of ALFRED C. LANE, State Geologist of Michigan.

[2] COHN: Die Algen des Karlsbader Sprudels, mit Rücksicht auf die Bildung des Sprudel Sinters: Abhandl. der Schles. Gesell., pt. 2, Nat., 1862, p. 35.

[3] WEED: Formation of Travertine and Silicious Sinter by the Vegetation of Hot Springs. U. S. Geol. Surv., IX, Ann. Rept., p. 619, 1889.

The ultimate source of this material, except the vegetable matter, is, undoubtedly, the clays of glacial deposits and like disintegrated rock-masses. These clays are rich in finely divided limestone and in the softer rock-forming minerals, some of which contain calcium compounds. Percolating water, containing dissolved carbon dioxide, the so-called carbonic acid gas, readily dissolves the calcium and other metallic salts up to a certain limit. The water with the dissolved matter in it runs along underground until an outlet is reached and issues in the form of a spring. This, in turn, uniting with other springs forms a stream which runs into a lake, carrying along with it the greater part of its mineral load. If the amount of carbon dioxide contained in the water is considerable, some of it will escape on reaching the surface, because of decrease of pressure, and with its escape, if the saturation point for the dissolved mineral matter has been reached, a part of this matter must be dropped in the form of a fine powder, as the water runs along over the surface. Theoretically, then, some, if not a great part of the dissolved matter, should be thrown down along the courses of the streams which connect the original outlets of the water from calcareous clays and lakes where marl occurs, and we should find the marl occurring in small deposits along these streams wherever there is slack water. Moreover, we should expect the waters of these springs and streams to show more or less milkiness on standing exposed to the normal pressure of the atmosphere at usual temperatures. Actually, however, none of these phenomena have been noted, and we infer that there is not a large amount of calcium dioxide, and not an approach to the saturation point for calcium bicarbonate, in the springs and streams feeding marly lakes.

We are then left, among others, the following alternatives, explanatory of marl formation: (1) The marl is not being formed under existing conditions, but has been formed in some previous time when conditions were not the same as now. (2) The amount of dissolved salts is so small that the saturation point is not approached until after the lakes are reached and the slow evaporation and the reduction of the amount of dissolved carbon dioxide in the water brings about deposition of the mineral salts. (3) Some other cause, or causes, than the simple release from the water of the solvent carbon dioxide must be sought.

The first of these suggestions is met by the fact that marl is found in lakes at and below the present level of the water, and that it extends in most of them to, or even beyond, the very edge of the marshes around the lakes, and over the bottom in shallow parts of living lakes, even coating pebbles and living shells. (2) The water of lakes with swift flowing and extensive outlets, such as most of our marly lakes have, is changed so rapidly that little if any concentration of a given volume of water would occur while it was in the lake, and there is no probability that any of the lakes visited by the writer have ever been without an outlet. Indeed, many of them have outlets which occupy valleys which have been the channels of much larger streams than the present ones. Moreover, definite measurements which, however, are subject to further investigation, have been made, which show that the volume of water flowing out of these lakes is practically the same as that flowing into them, *i. e.*, the loss by evaporation is too small a factor to be taken into account. Farther, recent investigations[1] have shown that calcium, as the bicarbonate, is soluble to the extent of 238 parts in a million, in water containing no carbon dioxide. As most of our natural waters, even from living clays, contain no more than this amount of salt, even when they carry considerable free carbon dioxide, and many analyses show a less amount of it, the fact becomes plain that even if the carbon dioxide were all lost there would be no precipitation from this cause. (3) Considering these objections as valid it seems fitting to examine into the possibility of the plant and animal organisms living in the waters of the lakes being the agents which bring about the reduction of the soluble calcium bicarbonate to the insoluble carbonate even in waters low in the amount of dissolved mineral matter, and containing considerable carbon dioxide. That mollusks can do this is shown by the fact, which has frequently come under the writer's notice, that the relatively thick and heavy shells of species living in fresh water are often partly dissolved and deeply etched by the action of carbonic acid after the animals have, by their processes of selection, fixed the calcium carbonate in their tissues, precipitating it from water so strongly acid and so free from the salt that re-solution begins almost immediately. No natural water seems so free from calcium salts that some species of mollusks are not able to find enough of the necessary mineral matter to build their characteristic shells.

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[1] TREADWELL and REUTER: Ueber die Loeslichkeit der Bikarbonate des Calciums und Magnesiums. Zeitschrift für Anorganish-Chemie, Vol. 17, 1898, p. 170.

While some limited and rather small deposits of marl are possibly built up, or at least largely contributed to, by molluscan and other invertebrate shells, the deposits which are proving commercially valuable in the region under consideration, do not contain recognizable shell fragments in any preponderance, although numerous nearly entire fragile shells may be readily washed or sifted from the marl. The conditions under which marl is found are such that the grinding of shells into impalpable powder, or fine mud, by strong wave action is improbable, if not impossible, for exposed shores and shallow water of considerable extent are necessary to secure such grinding action, and these are not generally found in connection with marl.

We are, then, reduced to the alternative of considering the action of plants as precipitating agents for the calcium salts. It has been shown already that plants generally become incrusted with mineral matter in our marly lakes, and it is easy to demonstrate that the greater part of the material in the incrustation is calcium carbonate. It is also easy for a casual observer to see that the deposit is not a true secretion of the plants, for it is purely external, and is easily rubbed off the outside of the plants in flakes, while the tissues beneath show no injury from being deprived of it, and again, as has already been pointed out, the same species of plants in some sections of the country do not have any mineral matter upon them. The deposit is formed incidentally by chemical precipitation upon the surface of the plants, probably only upon the green parts, and in performance of normal and usual processes of the plant organism.

All green plants, whether aquatic or terrestrial, take in the gas, carbon dioxide, through their leaves and stems, and build the carbon atoms and part of the oxygen atoms of which the gas is composed into the new compounds of their own tissues, in the process releasing the remainder of the oxygen atoms. Admitting these facts, which are easily demonstrated by any student of plant physiology, we have two possible causes for the formation of the incrustations upon plants.

If the calcium and other salts are in excess in the water, and are held in solution by carbon dioxide, then the more or less complete abstraction of the gas from the water in direct contact with plants, causes precipitation of the salts upon the parts abstracting the gas, namely, stems and leaves. But in water containing amounts of the salts, especially of the calcium bicarbonate, so small that they would not be precipitated if there were no carbon dioxide present in the water at all, the precipitation may be considered a purely chemical problem, a solution of which may be looked for in the action upon the bicarbonates, of the oxygen set free by the plants. Of these calcium bicarbonate is the most abundant, and the reaction upon it may be taken as typical and expressed by the following chemical equation:

$$\mathrm{CaH_2\,(CO_3)_2 + O = H_2O + CaCO_3 + CO_2 + O}\quad \left.\begin{matrix}\text{calcium}\\ \text{bicarbonate}\end{matrix}\right\} + \text{oxygen} = \text{water} + \left.\begin{matrix}\text{calcium}\\ \text{carbonate}\end{matrix}\right\} + \left.\begin{matrix}\text{carbon}\\ \text{dioxide}\end{matrix}\right\} + \text{oxygen}\ ,$$

in which the calcium bicarbonate is converted into the normal carbonate by the oxygen liberated by the plants, and both carbon dioxide and oxygen set free, the free oxygen possibly acting still farther to precipitate calcium monocarbonate.

It is probable that the plants actually do precipitate calcium carbonate, both by abstracting carbon dioxide from the water and by freeing oxygen, which in turn acts, while in the nascent state, upon the calcium salt and precipitates it, but in water containing relatively small amounts of calcium bicarbonate the latter would seem to be the probable method.

The calcium salt is deposited in minute crystals, and by the aggregation of these crystals the incrustation is formed on the plants. The crystals are distinguishable as such only for a short time on the newer growths of plants, but the incrustations are said to show a recognizable and characteristic crystalline structure when examined in thin section under a compound microscope with polarized light.

Not all aquatic plants in the same lake seem equally active in the precipitation of mineral matter. Not even all species of the same genera, even when growing side by side, will be coated equally, a fact which seems to indicate some selective metabolic processes not understood. Considering the precipitation of calcium carbonate by plants as established, even if the exact physiological and chemical processes by which this precipitation is brought about, are not yet worked out fully, it is still necessary to consider the constancy of the action and the sufficiency of the agency to produce the extensive deposits of marl which are known.

If one confines his studies simply to the seed-producing plants and other large vegetable forms which are conspicuous in lakes during the summer season, while he will find them covered with a thin coating of manifestly calcareous matter, he will at once be convinced that such work as these plants are doing is but a small factor in the total sedimentation of the lake. On the other hand, if a visit be made to a lake in early spring or late fall, all plants of the higher types will not be found, so that it becomes apparent that this agency is merely a seasonable one and works intermittently. Farther study of the plants of the same body of water, however, shows that the algæ, the less conspicuous and entirely submerged plant organism, must be taken into account before we finally abandon plants as the agents of precipitation. Of these, two groups, differing widely in structure, habits, and method of precipitation, will be found. The first and most conspicuous, and probably the most important as well, is the Characeæ or Stoneworts. These plants are well known to botanists, and may readily be recognized by their jointed stems, which have at each joint a whorl of radiating branches, which are also jointed. In some species the stems and branches are covered with a thick coating of mineral matter, are almost white, and very brittle because of this covering. These plants not only grow near the surface in shallow water, where it is unoccupied by other plants, but in the deeper parts as well of our ponds and lakes, and, as they thrive where light is feeble, they continue to grow throughout the year, although in winter they must grow less rapidly than in summer, because ice and snow on the surface of the lakes make less favorable light conditions.

The sufficiency of these plants alone to fix and deposit calcium carbonate in large quantities is indicated by the following: In November 1899 the writer collected a large mass of plants of Chara sp?, from which five stems with a few branches were taken at random and without any particular care being taken to prevent the brittle branches from breaking off. The stems were each about 60$^{cm}$ long, and after being dried for some days they were roughly ground in a mortar and dried for one half hour at 100° C., dried and weighed until the weight was constant. The weight of the total solid matter obtained in this way from five plants was 3.6504 grams, 0.73 grams per plant. This was treated with cold hydrochloric acid diluted, twenty parts of water to one of acid, filtered, washed, and the residue dried at 100° C., on a weighed filter paper, until weight was constant. The weight of insoluble matter was 0.5986 grams; of the total soluble matter 3.0518 grams, or .6103 grams per plant. In the lake from which the material analyzed was derived from 50 to 80 plants were counted to the square decimeter of surface in the Chara beds.

A partial quantitative analysis of material from the same source, but using stronger acid to affect solution (hydrochloric acid, diluted with four parts of water), gave the following results:

| | |
|---|---|
| Insoluble residue | 11.19 % |
| Iron and aluminum oxides | 0.722 |
| Calcium carbonate | 76.00 |
| Magnesium carbonate | 2.359 |
| Soluble organic matter obtained by difference | 9.279 |

The composition of the insoluble residue was obtained by heating the residue to redness in a platinum crucible for one half hour, and the 11.19 per cent. of this matter was found to consist of:

| | | |
|---|---|---|
| Combustible and volatile matter | 9.243 % | = 82.6 % |
| Mineral matter | 1.947 | = 17.4 |

The mineral matter was found to be:

| | | |
|---|---|---|
| Silica | 1.787 % | = 92.4 % |
| Not determined | .160 | = 7.6 |

Microscopic examination showed the silica to be largely composed of whole and broken tests of diatoms, minute plants which secrete silicious shells and attach themselves to the Chara stems and branches.

The mineral matter obtained in this analysis, reduced to parts per hundred, gives the following:

| | Per cent. |
|---|---|
| Calcium carbonate | 93.76 |
| Magnesium carbonate | 2.93 |
| Silica and undetermined mineral matter | 2.40 |
| Iron and aluminum oxides | .89 |

This, with a small decrease in the mineral matter and a small amount of organic matter added, would be the composition of ordinary marls, and would be a suitable sample to consider in connection with Portland cement manufacture.

The large amount of silica may be explained by the fact that the material analyzed was collected at a season when diatoms are especially abundant.

It may be well to call attention to the fact that in many marls, especially those of large deposits, which the writer has examined chemically, the silica has been found to be in the form of diatom shells, and hence, because of the small size and great delicacy of these structures, it is available as a source of silica for calcium silicate in cement making. If such deposits as are made up largely of diatom shells were adjacent to marl beds, it is possible they might be considered as clay and be used in cement making.

From the above considerations, it is evident that both because of the quality and quantity of its works, Chara may be considered an important agent in marl production, and it only becomes necessary to account for the chalky structure of the deposits to make the chain of evidence complete. All algæ are plants of very simple structure, without tough or complicated tissues. Chara stems and branches are made up of aggregations of thin-walled cells, and when the plants die the cell walls must rapidly decay and the residue of lime be left. In a laboratory experiment to determine this factor, it was found that a mass of the broken-up plants placed in the bottom of a tall glass vessel filled with water became decomposed very quickly, giving the characteristic odor of decaying vegetable matter, and after a few weeks all organic matter had disappeared, leaving the incrustations in tubular, very brittle, fragments. In studying the structure of marl, the writer has found that near the top of the beds there is usually a "sandy," or even a coarsely granular structure. This is noticeable, at times, at all depths from which the samples are taken, *i. e.*, in some cases it extends through the bed. Close examination of such marl shows that this coarseness is due to the remains of the characteristic Chara incrustations, and that the "sand" and other course material is made up of easily identifiable fragments of the coatings of stems and branches of the plant. The presence of such coarse matter near the top of the beds may be considered due to sorting action of the waves, and such surface currents as may be caused in ponds and small lakes, in shallow water, by wind action. If these agents are effective in producing the coarser parts of the deposits they may be also considered so in connection with the finer parts as well, for the matter produced by the breaking and grinding up of fragments is held in suspension for a longer or shorter time, carried about by currents, and finally sinks to the bottom in the quieter and deeper parts of the lakes.

Chara may also be looked upon as an important agent in giving the peculiar distribution to marl which has been noticed by every one who has "prospected" beds of material. The fact is frequently noticed that beds of several, and even as much as twenty or more, feet in thickness will "run out" abruptly into beds of "muck," or pure vegetable débris, of equal thickness. This distribution may show that up to a certain time conditions unfavorable to the growth of Chara are favorable to other plants obtained, until a depth of water was reached at which Chara was able to occupy the bed of muck, covering it from the bottom up, and holding the steep slope of the muck in place by mechanically binding it there by its stems and the root-like bodies by which it is connected with the mud. From the time when the Chara began its occupation of the muck the amount of organic matter left would decrease, and the amount of calcareous deposit would increase, until the latter predominated. The disturbing factors of currents and waves can be disregarded, for these abrupt unions of marl and muck are found, so far as the observations of the writer go, in most sheltered places, and not where either currents or waves could ever have operated with any force or effectiveness. Moreover, in a lake where the marl is evidently now actively extending, the slope was observed to be nearly perpendicular, and the steep banks thus formed were thickly covered with growing Chara, to the exclusion of other large forms of plant life, and the lower parts of the growing stems were buried in mud which was mainly pure marl.

In regard to the species of Chara which seems to be the active agent in precipitation in the lakes of central Michigan, it is the form commonly known as *Chara fragilis*, but it is probable that careful study of the species throughout the range of the marl will reveal, not a single form, but a number of allied species, engaged in the same work. It may be well to suggest that in lakes to which much silt is brought by inflowing streams, or which have exposed shores where the waves are constantly cutting and stirring up rock débris, the more slowly accumulating marls will be either so impure as to be worthless, or so obscured as to escape notice altogether, even where Chara is abundant. It may also be pointed out that shallow water, strong light, and a bottom of either clay, sand, or muck, present conditions favorable for the growth of the higher vascular plants, and that these cause such rapid accumulation of vegetable débris that the calcareous matter may be hidden by it, even when Chara is a well-marked feature of the life of a given lake.

Another plant form, like Chara an alga, but of a much lower type, which is concerned in the formation of marl is one of the filamentous blue-green algæ, determined by Dr. Julia W. Snow, of the University of Michigan, to be a species of Zonotrichia, or some closely related genus.

The work of this species is entirely different in its appearance from that of Chara, and at first glance would not be attributed to plants at all. It seems to have been nearly overlooked in this country at least by botanists and geologists alike, as but a single incidental reference to it has been found in American literature.[1] Curiously enough, however, material very similar, if not identical, to that under consideration has been described from Michigan in an English periodical devoted to Algæ.[2] In this the alga is identified as *Schizothrix fasciculata* Goment. As comparison of material is not possible at the present time, the plant under consideration is here tentatively called Zonotrichia. The plant grows in relatively long filaments, formed by cells growing end to end, and as they grow, the filaments become incased in calcareous sheaths. The feature of the plant which makes it important in this discussion, however, is its habit of growing in masses or colonies. The colony seems to start at some point of attachment, or on some object like a shell, and to grow outward radially in all directions, each filament independent of all others and all precipitating calcium carbonate tubules. The tubules are strong enough to serve as points of attachment for other plants, and these add themselves to the little spheroid, and entangle particles of solid matter, which in turn are held by new growths of the lime-precipitating Zonotrichia, and thus a pebble of greater or less size is formed which to the casual observer is in no wise different from an ordinary water-rounded pebble. These algal calcareous pebbles show both radial and concentric structure and might well be taken for concretions formed by rolling some sticky substance over and over in the wet marl on which they occur but for the fact that a considerable number of them show eccentric radial arrangement, and that the shells of accretion are likewise much thicker on one side than on the other, and finally, because the side which rests on the bottom is usually imperfect and much less compact than the others. The pebbles are characteristically ellipsoidal in shape. The radial lines, noticeable in cross sections of the pebbles, are considered by the writer to be formed by the growth of the filaments, while the concentric lines probably represent periods of growth of the plants, either seasonal or annual. Included within the structure are great numbers of plants, besides the calcareous Zonotrichia, among them considerable numbers of diatoms, and it is probable that a large part of the algal flora of a given lake would be represented by individuals found in one of these pebbles. It is probable that to a certain extent they disintegrate after the plants cease to grow, for they are never very hard when wet. It is possible to recognize them, as lumps of coarser matter, even in very old marl, and the writer has identified them in marl from Cedar Lake, Montcalm county, Mich., which was taken from a bed a foot or more above, and several rods away from, the lake at its present level. From the fact that these pebbles have been found in four typical marl lakes in different parts of Michigan (in Zukey Lake, by Dr. A. C. Lane, who was struck with their peculiar character) and have been reported from a number of others by marl hunters, it is probable that they have a wide distribution in the state and are constant if not important contributors to marl beds. It may be said in passing that the limy incrustations which are found upon twigs, branches, shells, and other objects in lakes and streams, and called generally "calcareous tufas," are of similar origin and are formed by nearly related, if not by the same, plants that form the pebbles.

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[1] McMillan: Minn. Plant Life, 1899, p. 41.

[2] G. Murray: Phycological Memoirs No. XIII, 1895, p. 1, Pl. XIX.

Studies have been begun by the writer to solve, if possible, some of the questions which have arisen in connection with the statements embodied in this paper, but enough has already been done to show that these forms of fresh-water algæ are important lime-precipitating agents now, and to suggest the possibility that in all likelihood they have been more active in former geological times, and that, as has been suggested again and again by botanists, the formation of certain structureless limestones, and tufa deposits may have been due to their work.

CHARLES A. DAVIS.

ALMA COLLEGE,
September 1, 1900.